Catalytic fast pyrolysis of biomass:

From lab-scale research to industrial applications

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Biosystems Engineering

Faculteit Bio-ingenieurswetenschappen
Faculty of Bioscience Engineering

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Questions related with the CFP of biomass:

- Production of drop-in biofuels/chemicals ***vs.*** the integration of the product of CFP with the existing petroleum refineries
- In situ CFP ***vs.*** ex situ CFP
- The accumulation of biomass originated ash within the system?

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Introduction

The problem:

Physical and chemical properties of crude bio-oil make it a poor precursor for the production of fuels and chemicals. Bio-oil needs significant upgrading to become compatible with the refinery intermediates.

Biomass

Primary processing

Liquid intermediate

Oil Refinery

Can handle liquid feedstocks with ca. 10 wt.% of oxygen

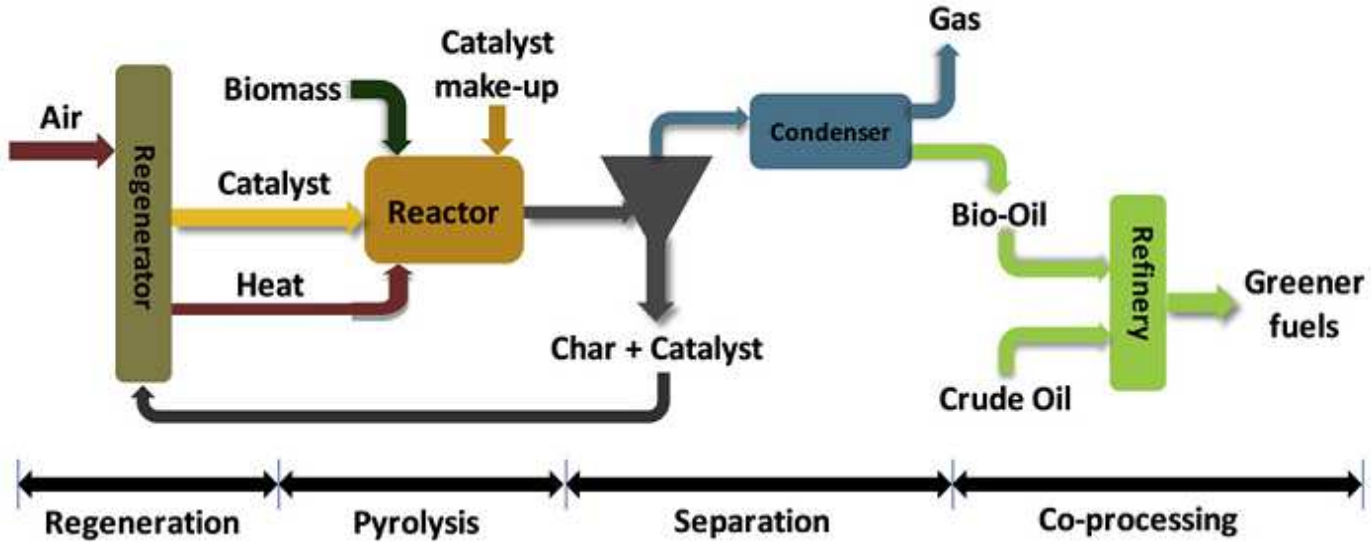
Secondary processing

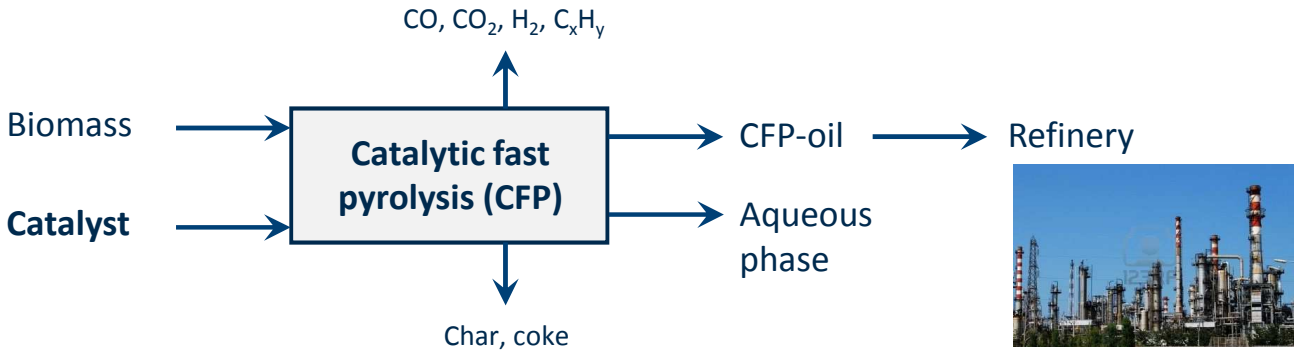
Chemicals

Fuels

The aim:

To develop a process to convert lignocellulosic (non-food) biomass into a bio-crude oil with more desirable properties that can (partially) replace petroleum crude in the existing refineries.

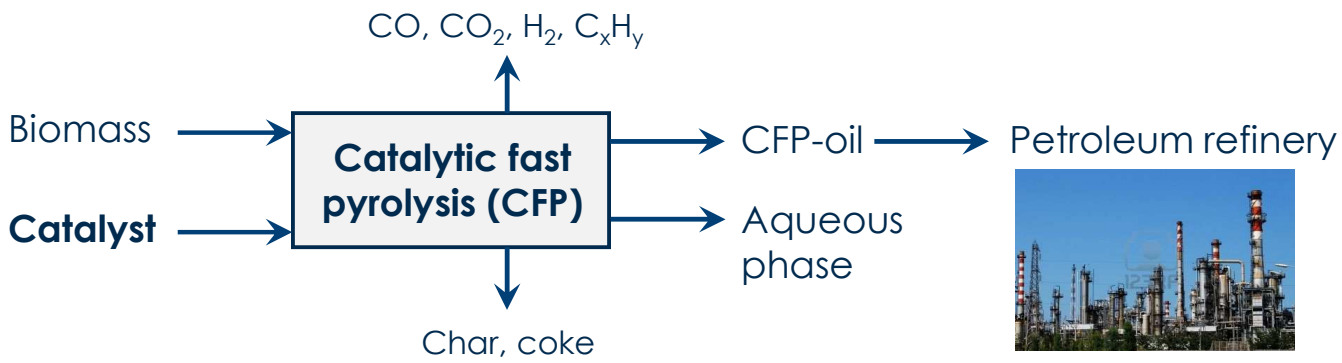




Goal of CFP of biomass: Optimize a process and develop suitable catalysts to selectively remove oxygen from biomass pyrolysis vapours prior to condensation to improve bio-oil quality.

Catalytic Fast Pyrolysis:

Pyrolysis carried out in the presence of a catalyst (in situ) or pyrolysis followed by catalytic processing of vapors (ex situ).



Objectives:

- Removal of bio-oil oxygen in the form of H_2O, CO and CO_2

$$CH_{1.46}O_{0.67} \rightarrow aC_xH_y + bCO_2 + cCO + dC + eH_2O$$

- Increased production of the target compounds (*e.g.* aromatics, phenolics)
- Decreased acidity in liquid product (TAN < 10)
- Retaining the energy in the liquid product
- Producing a liquid product with a higher carbon content and heating value
- Improve stability

Challenges in the design and operation of continuous CFP processes

- The effect of the operation mode
- Lifetime and deactivation of the catalyst
  a. The effect of repeated catalyst regeneration
  b. The effect of biomass ash
- Proposed process configurations

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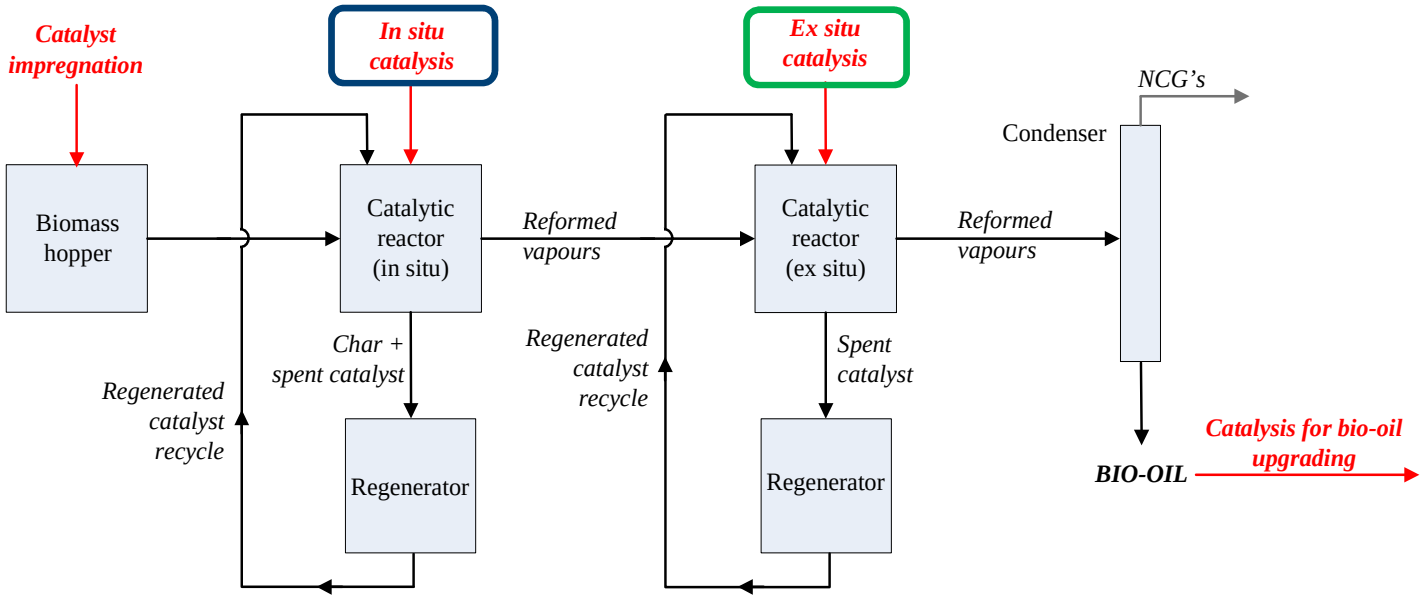
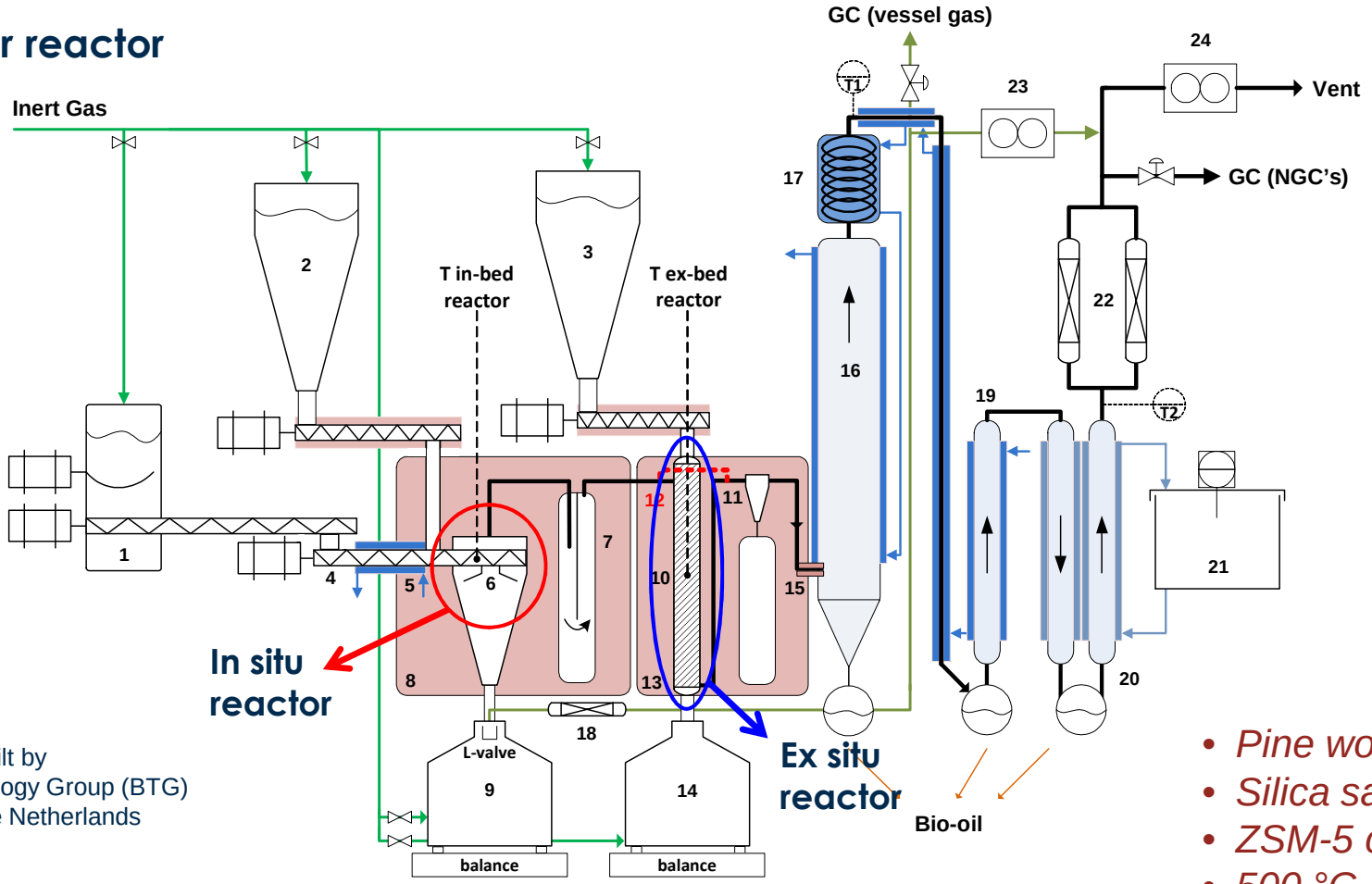


Options for the addition of catalyst materials in a fast pyrolysis process.
Yildiz, G. (2015). Catalytic fast pyrolysis of biomass (Doctoral dissertation). Ghent University, Ghent, Belgium, 214 p.

- In situ catalysis:
  - Immediate attack of the released biomass volatiles
  - Catalyst can act as a process heat carrier
  - Char combustor in the pyrolysis process can be a catalyst regenerator
  - Temperature of catalysis is constant
  - Abrasion resistant catalyst is required
- Ex situ catalysis:
  - Flexibility in conditions of catalysis such as temperature, particle size and shape, reactor type, utilization of reactive gases (e.g. hydrogen)

The effect of the operation mode

- **Auger reactor**

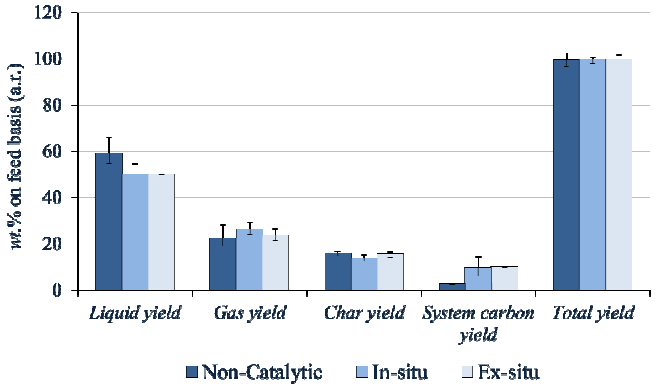


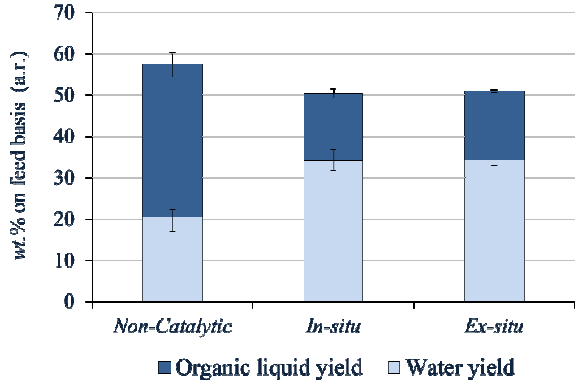
Designed and built by
Biomass Technology Group (BTG)
in Enschede, The Netherlands

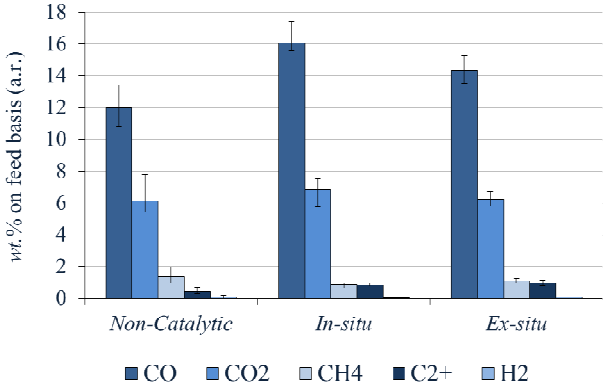
- *Pine wood*
- *Silica sand*
- *ZSM-5 catalyst*
- *500 °C*

Bench scale setup for (catalytic) fast pyrolysis of biomass.

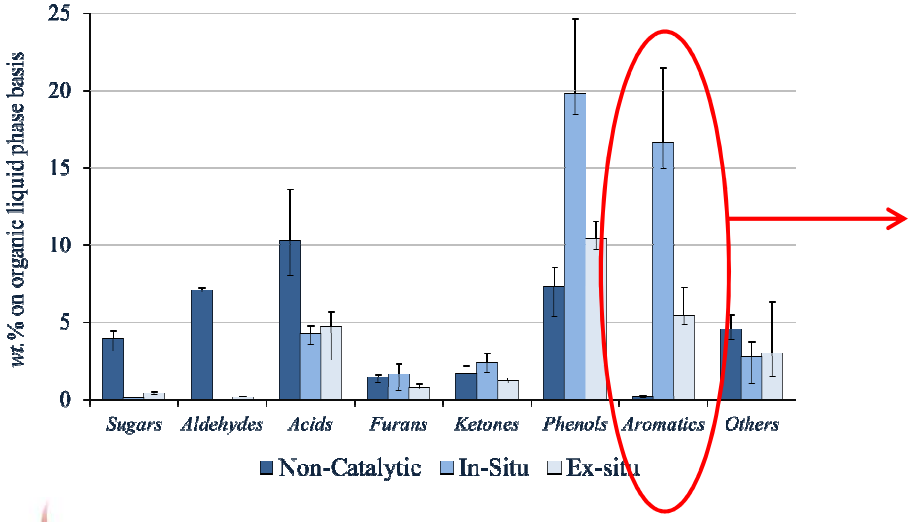
Product yields

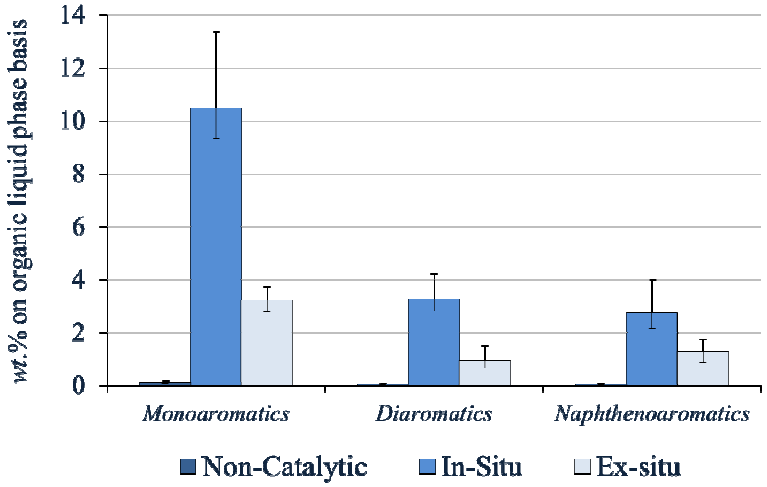






Liquid analyses (2D-GC/MS)





The effect of the operation mode – *Conclusions*

Similarities:

- The application of the catalyst resulted in a **significant decrease in the overall liquid yields in both cases**; they decreased *ca.* 9 wt.% for in- and ex situ CFP.
- The **yields of organic fractions of liquids (CFP-oil) in both cases were similar** (*ca.* 17 *wt.*%) and lower than that obtained from non-catalytic fast pyrolysis (37 *wt.*%).

Differences:

- **In situ CFP led to a higher yield in gas products** than ex situ CFP (26.2 *wt.*% vs. 23.9 *wt.*%).
- In both cases, the concentration of organic acids was decreased while **in situ CFP resulted in much higher selectivity to phenols and aromatic hydrocarbons than that of ex situ CFP.**
- Compared to the in situ mode, **ex situ mode consumed less catalyst** (more than a factor of 2) to reach the same catalyst-to-biomass ratio due to the variations in the catalyst feed rates.
- Literature suggests that the **ex situ option has less techno-economic risk and higher production rate**.

Reference:
Yildiz, G., Pronk, M., Djokic, M., van Geem, K. M., Ronsse, F., van Duren, R., & Prins, W. (2013). Validation of a new set-up for continuous catalytic fast pyrolysis of biomass coupled with vapour phase upgrading. Journal of Analytical and Applied Pyrolysis, 103, 343–351.

Challenges in the design and operation of continuous CFP processes

- The effect of the operation mode
- **Lifetime and deactivation of the catalyst**
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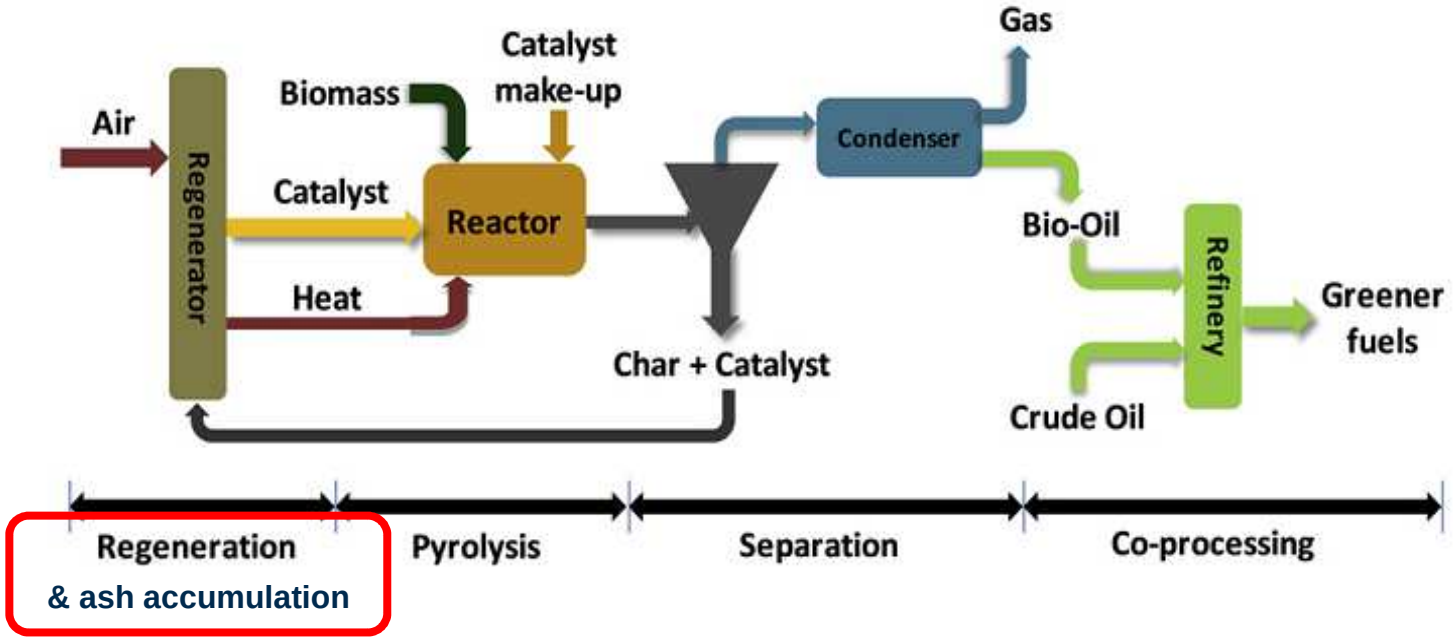
Lifetime and deactivation of a catalyst

The research question:

- What is the outcome of the long-term use of a catalyst in in situ CFP of lignocellulosic biomass?



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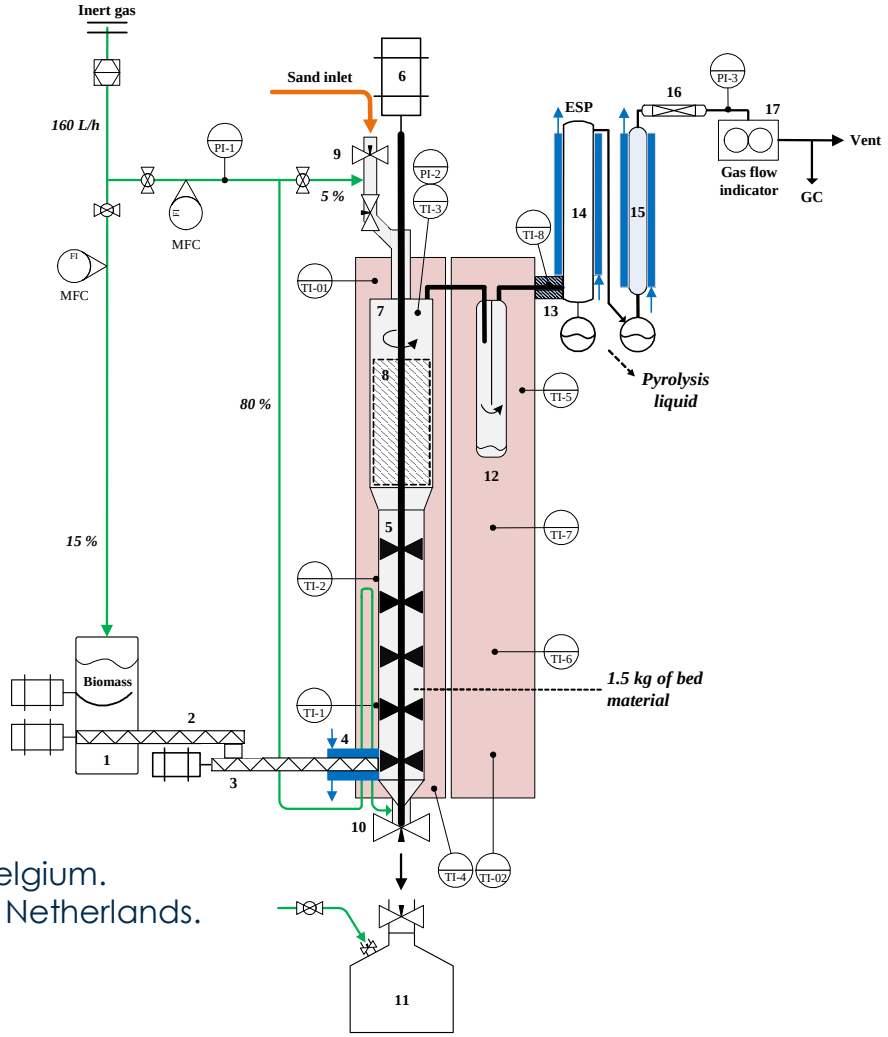
Mechanically stirred bed reactor



Designed in Ghent University, Belgium.
Built in University of Twente, The Netherlands.

- *Pine wood*
- *Silica sand*
- *ZSM-5 catalyst*
- *500 °C*

Bench scale setup for (in situ catalytic) fast pyrolysis of biomass.

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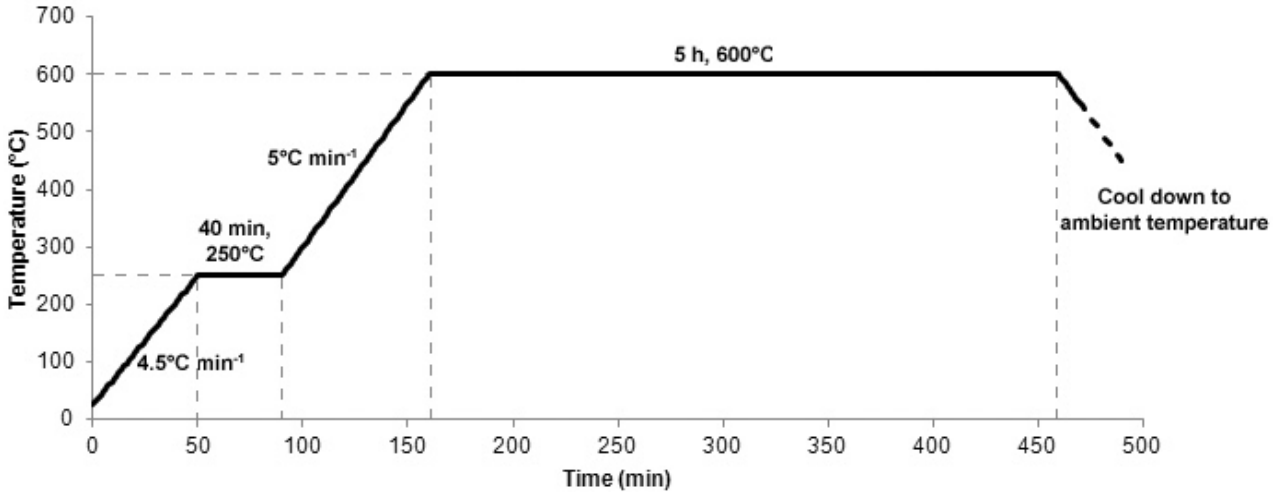
The effect of repeated catalyst regeneration

The performance of the catalyst under successive reaction/regeneration cycles was tested under realistic (harsh) conditions, such as:

1. mechanical mixing of the catalyst/sand bed during the pyrolysis runs, which promotes attrition and crushing of the catalyst particles;

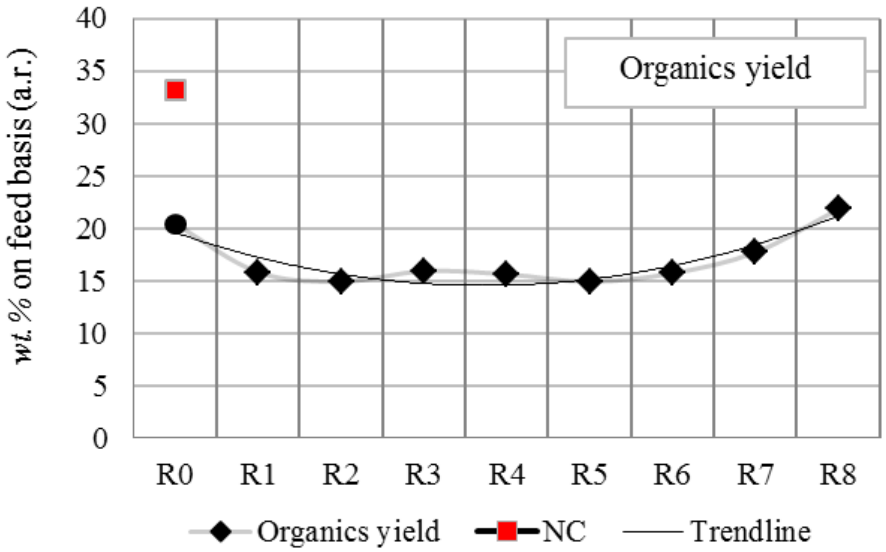
2. higher catalyst regeneration temperatures of 600 °C;

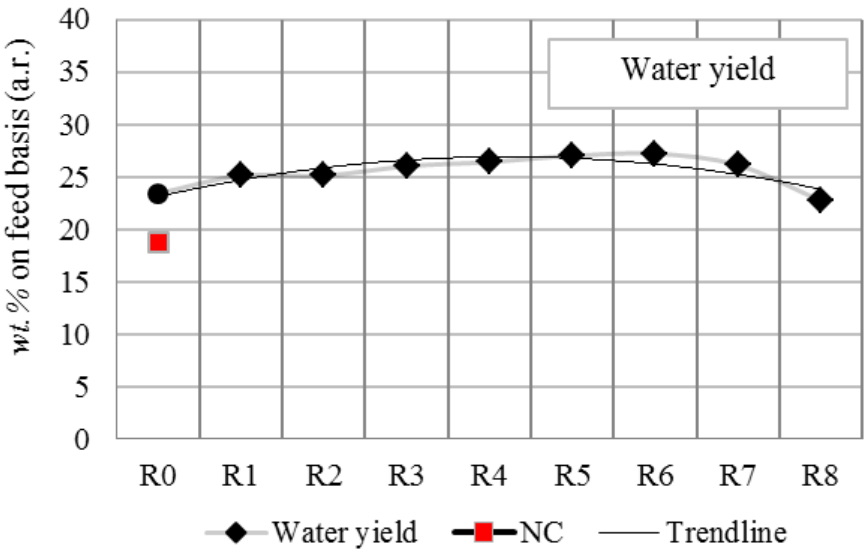
3. regeneration in the presence of the pyrolysis char, leading to the accumulation of biomass ash in the reactor bed material over the successive reaction/regeneration cycles.

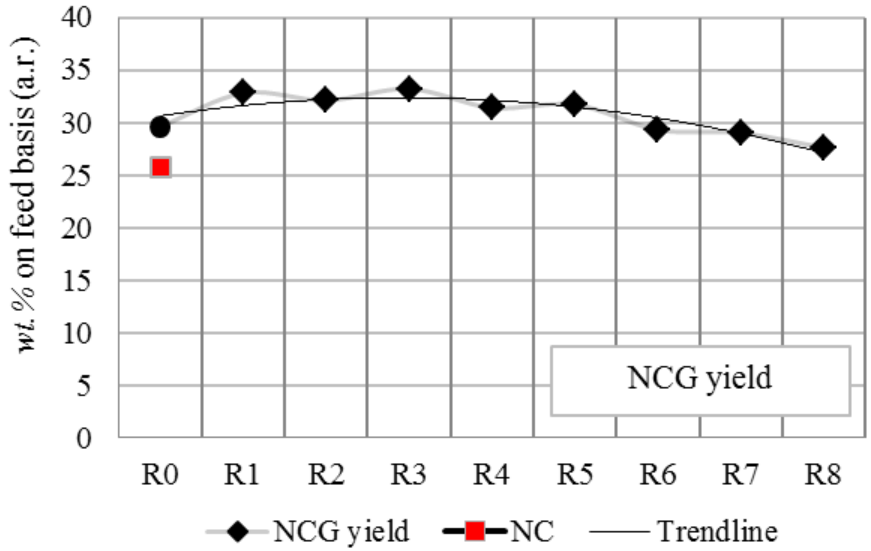


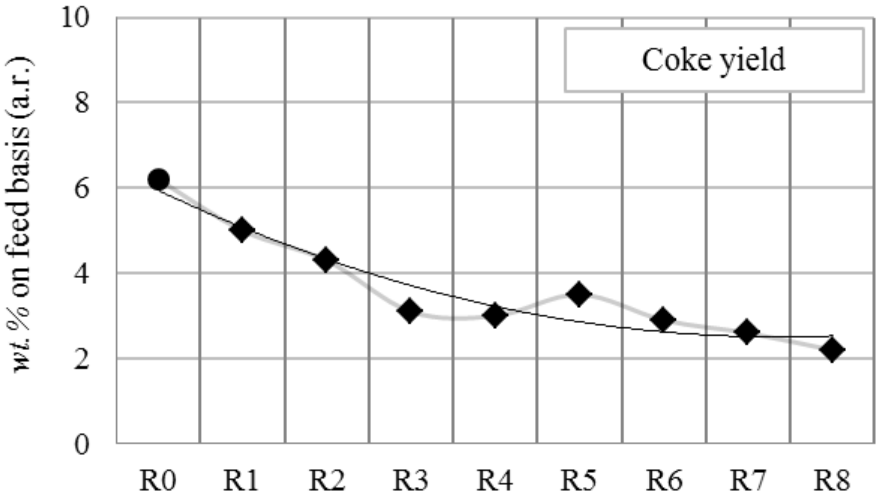
Temperature profile used for the regeneration of the catalyst.

The regeneration procedure was based on:
Aho, A.; Kumar, N.; Eranen, K.; Salmi, T.; Hupa, M.; Murzin, D.Y. *Process Saf. Environ.* **2007**, *85*, 473-480.

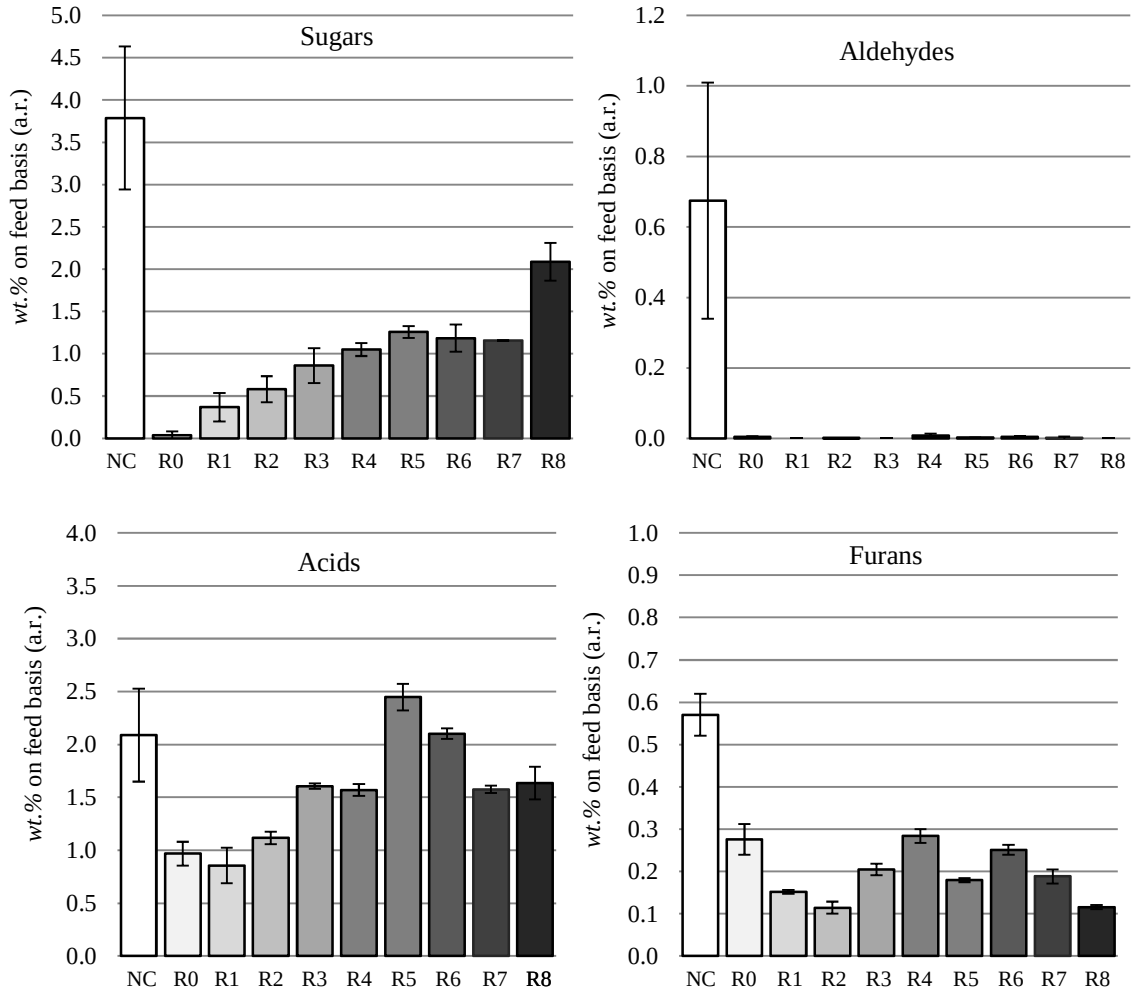




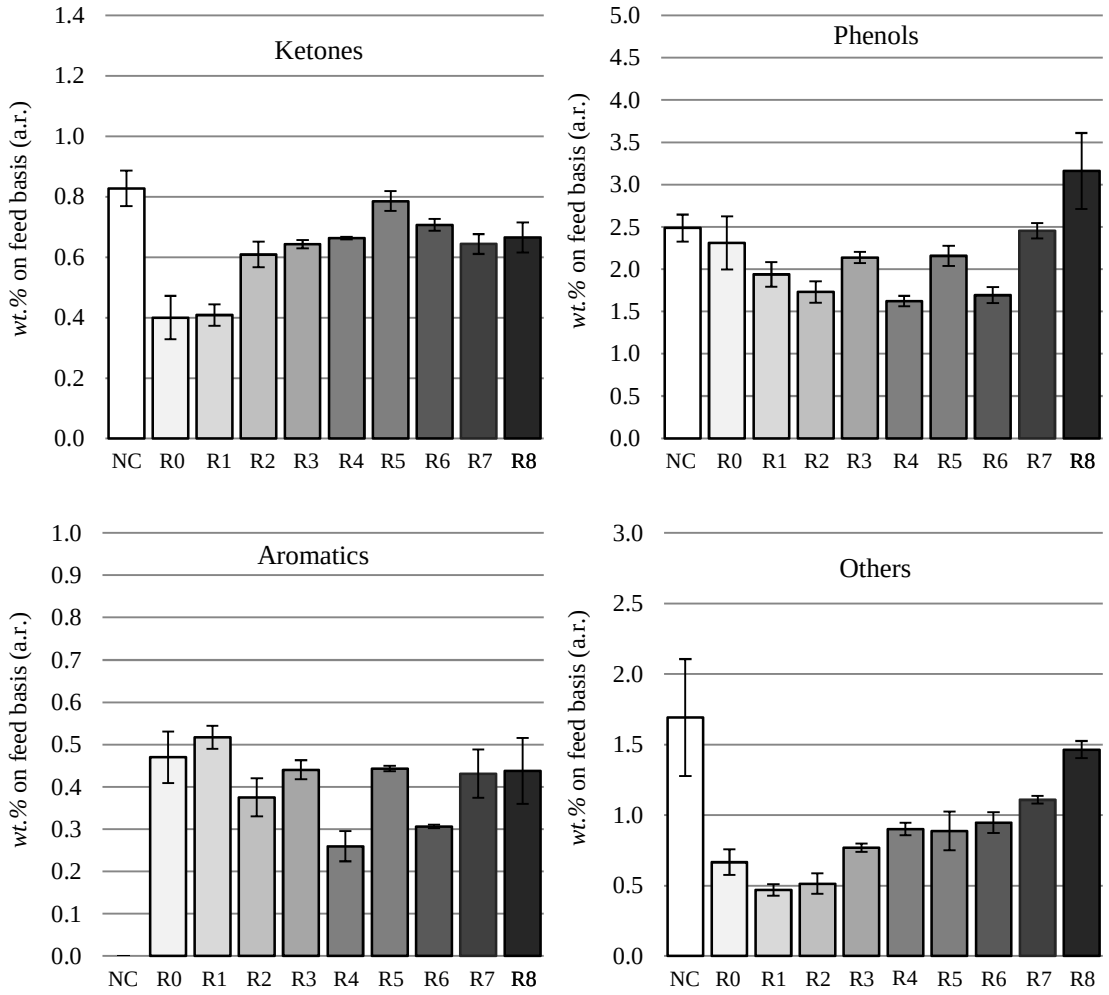




BET surface area analyses revealed that after eight reaction/regeneration cycles 63 % of the original surface area was lost.



Yildiz, G., Lathouwers, T., Toraman, H. E., van Geem, K. M., Marin, G. B., Ronsse, F., van Duren, R., Kersten, S. R. A., & Prins, W. (2014). Catalytic fast pyrolysis of pine wood: Effect of successive catalyst regeneration. Energy & Fuels, 28, 4560–4572.



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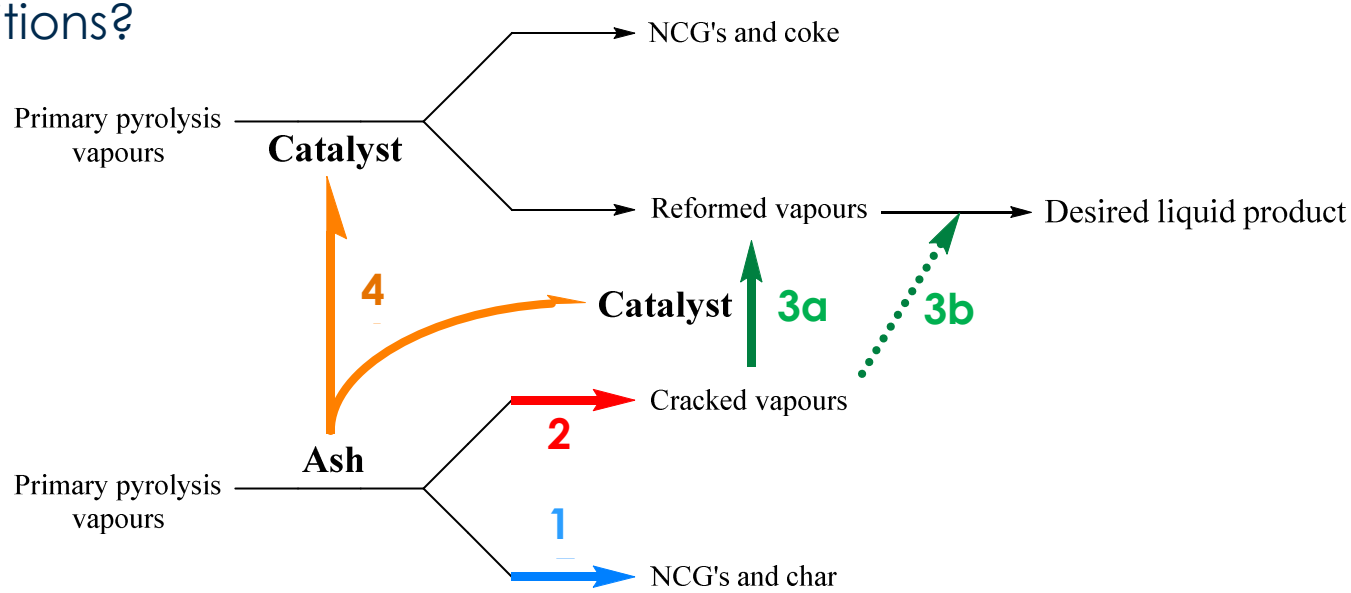
Research question:

- Is there any effect of biomass ash on the CFP product yields and compositions?

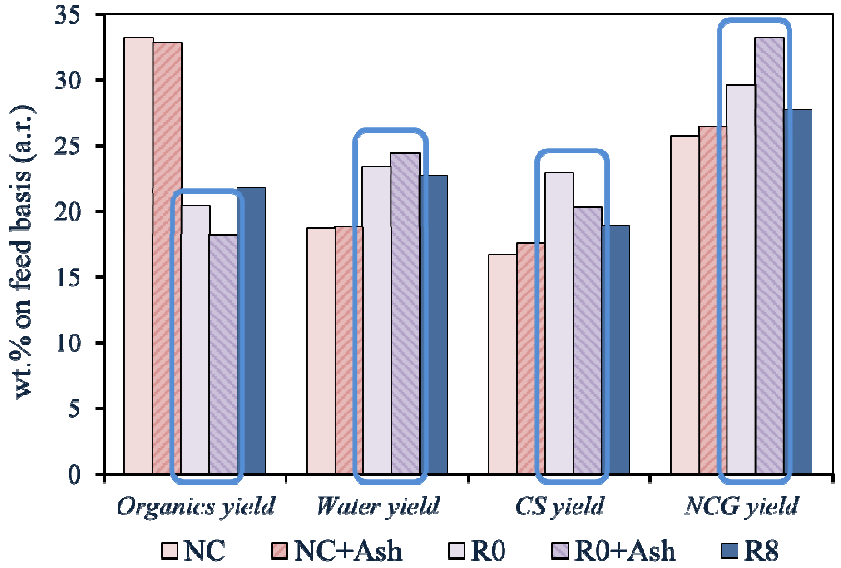


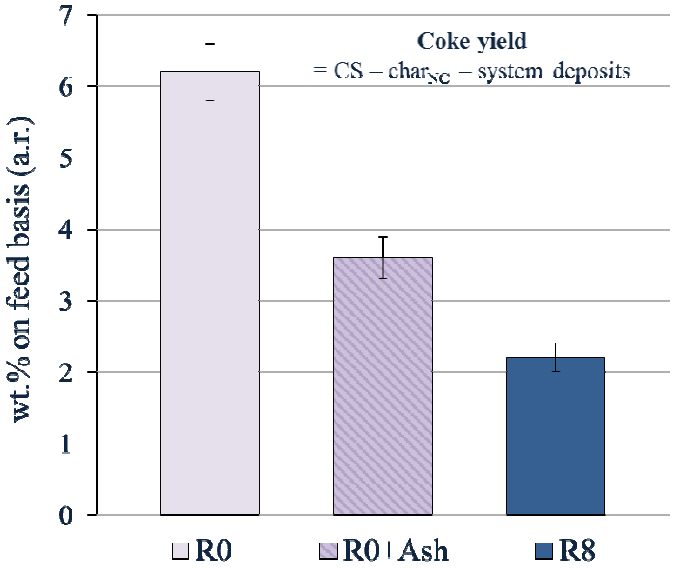
1 The catalytic effect of ash itself on the primary pyrolysis vapours results in the increased production of non-condensable gases (NCGs) and char;

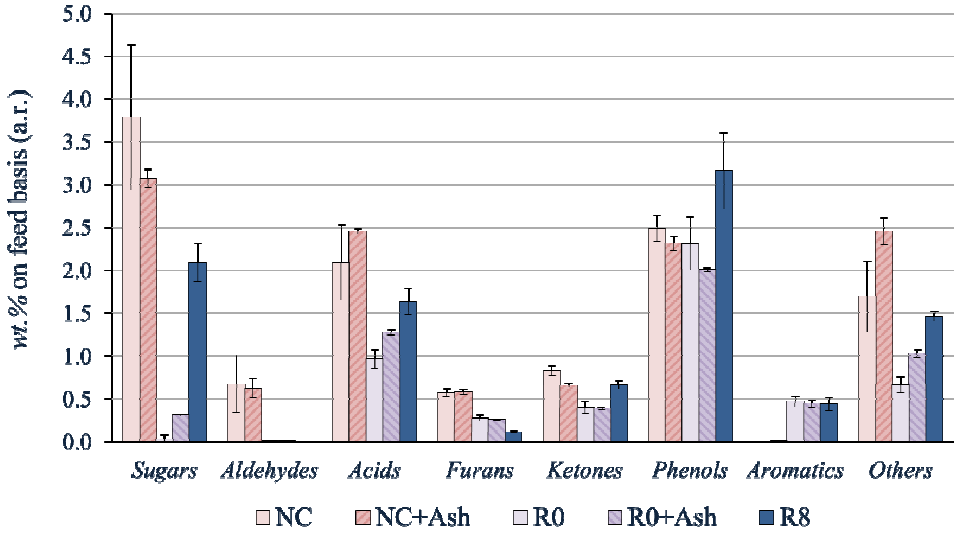
2 Ash may crack some larger vapour phase molecules inaccessible to the catalyst's interior, to smaller ones which are capable of entering the catalyst pores;

3 Cracked vapours may then either be further reformed by the catalyst **(a)** or not **(b)**;

4 Ash particles poison the catalyst and (negatively) affect the vapour conversion and the reaction chemistry.


wt.% on feed basis (a.r.)
35
30
25
20
15
10
5
0
Organics yield
Water yield
CS yield
NCG yield
NC
NC+Ash
R0
R0+Ash
R8


wt.% on feed basis (a.r.)
7
6
5
4
3
2
1
0
Coke yield
= CS – char$_{NC}$ – system deposits
R0
R0 + Ash
R8


wt.% on feed basis (a.r.)
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Sugars
Aldehydes
Acids
Furans
Ketones
Phenols
Aromatics
Others
NC
NC+Ash
R0
R0+Ash
R8

Lifetime and deactivation of a catalyst - *Conclusions*

- Trends in product yields showed that **the catalyst loses its activity throughout the successive reaction/regeneration cycles**.
- **Accumulated ash may affect the efficiency of the catalyst** by its influence on the composition of the primary pyrolysis vapours to be reformed by the catalyst.
- **Ash concentrations as low as *ca.* 3 *wt.*% relative to the amount of pine wood fed, and *ca.* 0.002 *wt.*% relative to the amount of bed material, were found sufficient to have a direct effect on the yield and composition of the catalytic fast pyrolysis products.**

References:

- *Yildiz, G., Lathouwers, T., Toraman, H. E., van Geem, K. M., Marin, G. B., Ronsse, F., van Duren, R., Kersten, S. R. A., & Prins, W. (2014). Catalytic fast pyrolysis of pine wood: Effect of successive catalyst regeneration. Energy & Fuels, 28, 4560–4572.*
- *Yildiz, G., Ronsse, F., Venderbosch, R., van Duren, R., Kersten, S. R. A., & Prins, W. (2015). Effect of biomass ash in catalytic fast pyrolysis of pine wood. Applied Catalysis B: Environmental, 168, 203–211.*

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How the problems related with the presence of 'biomass ash' and 'the successive catalyst regeneration' be overcome in CFP?

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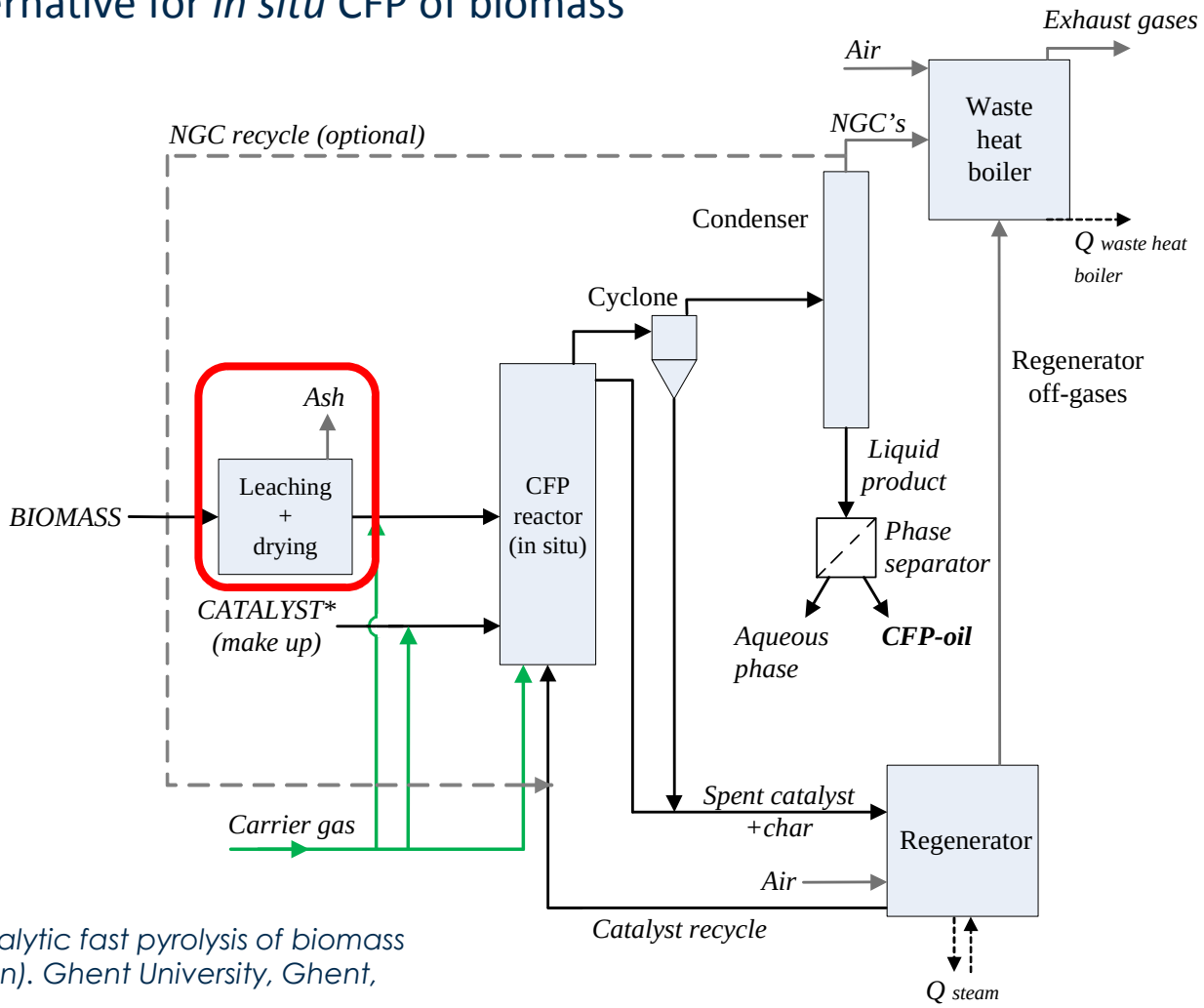
Option A

a process alternative for *in situ* CFP of biomass

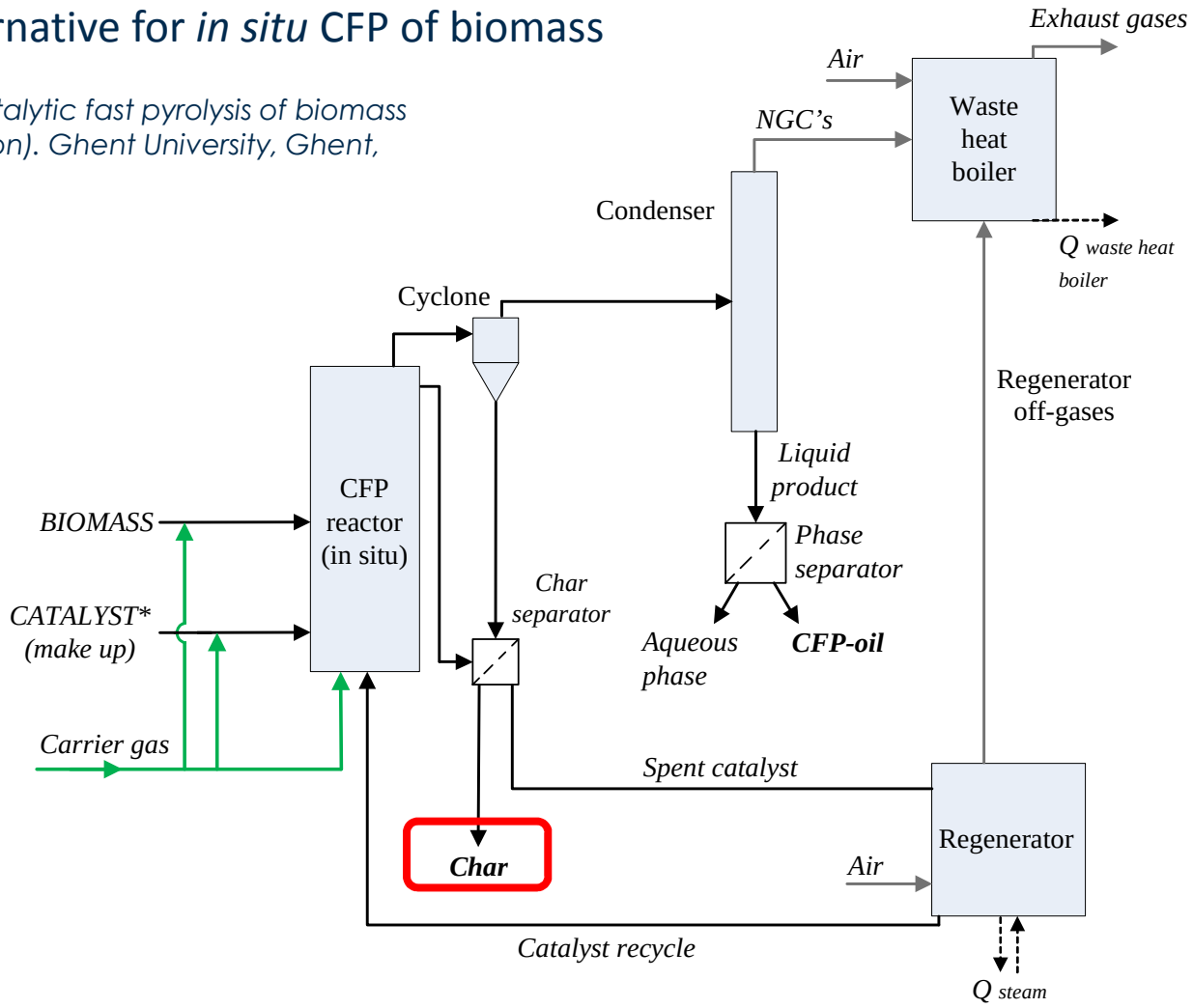


Yildiz, G. (2015). Catalytic fast pyrolysis of biomass (Doctoral dissertation). Ghent University, Ghent, Belgium, 214 p.

Option B

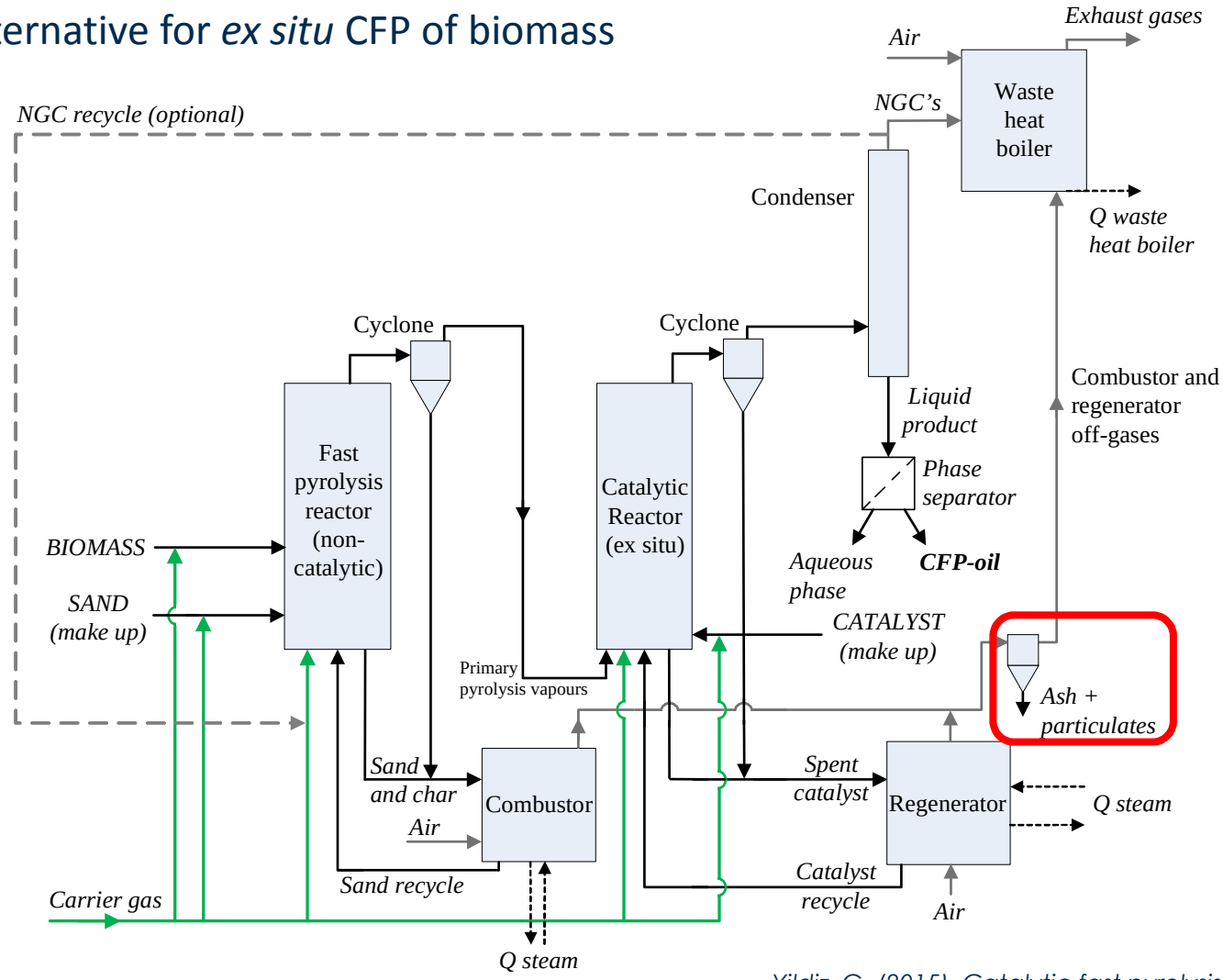
a process alternative for *in situ* CFP of biomass

Yildiz, G. (2015). Catalytic fast pyrolysis of biomass (Doctoral dissertation). Ghent University, Ghent, Belgium, 214 p.



Option C

a process alternative for *ex situ* CFP of biomass



Yildiz, G. (2015). Catalytic fast pyrolysis of biomass (Doctoral dissertation). Ghent University, Ghent, Belgium, 214 p.

Conclusions & remarks

- To overcome the drawbacks of biomass ash in case of the commercial/industrial scale CFP operation;
  - **the char** (which contains a vast majority of the biomass ash) **has to be physically removed from the catalyst before the regeneration step,**
  - or the **direct physical contact between the catalyst and the biomass must be prevented** by the utilization of ex situ processes.
- Future research should reveal whether the observed trends will persist after many more reaction/regeneration cycles, and **how long it takes for the catalyst to completely deactivate**.
- Strategies to reduce the minerals (*i.e.* biomass leaching, char removal) burden in the catalytic fast pyrolysis process could extend the lifetime of the catalyst.
- Reseach focused on the **improvement of the catalysts which are resistant to poisoning by ash minerals** can be considered.
- New catalyst formulations, improved catalyst regeneration procedures, improved reactor technologies and optimized process conditions are all possible strategies to further improve the result of CFP process.

Your questions are welcome.

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